

Supporting information

Impact of Cation- π Interactions on the Cell Voltage of Carbon Nanotube-based Li Batteries

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Figure S1. (a) and (b) are top views of Li⁺/Li internal and external adsorption in (4,4), (8,8), (10,10) SWNTS at the most stable H site, respectively. (c) is the side view of Li⁺/Li internal and external adsorption in (4,4), (8,8), (10,10) SWNTS at H site.

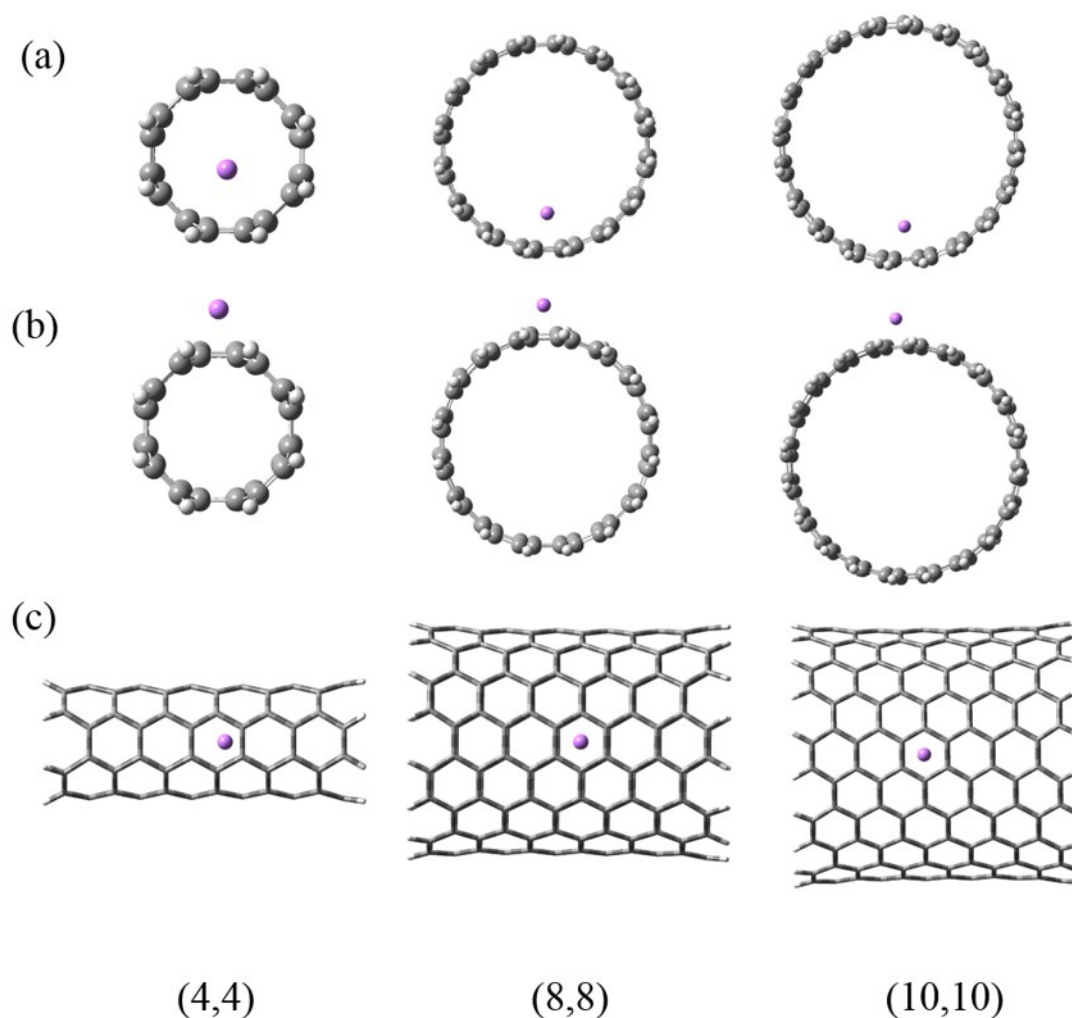
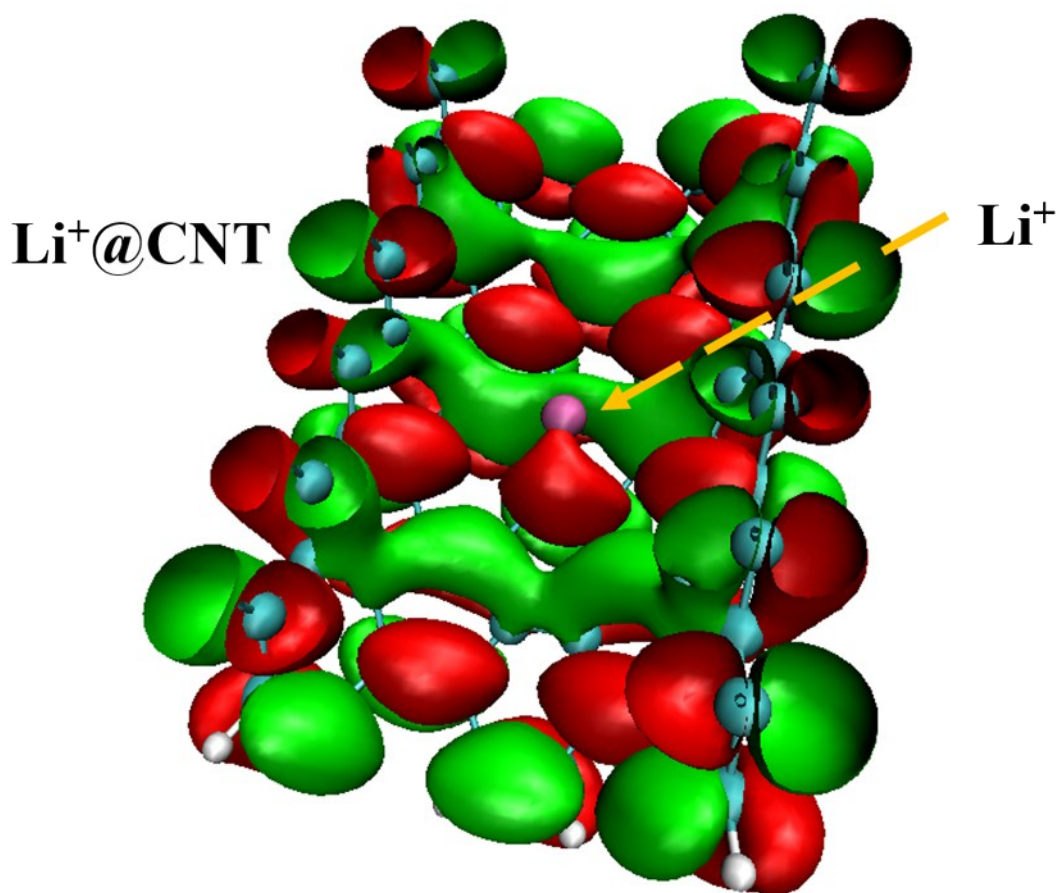
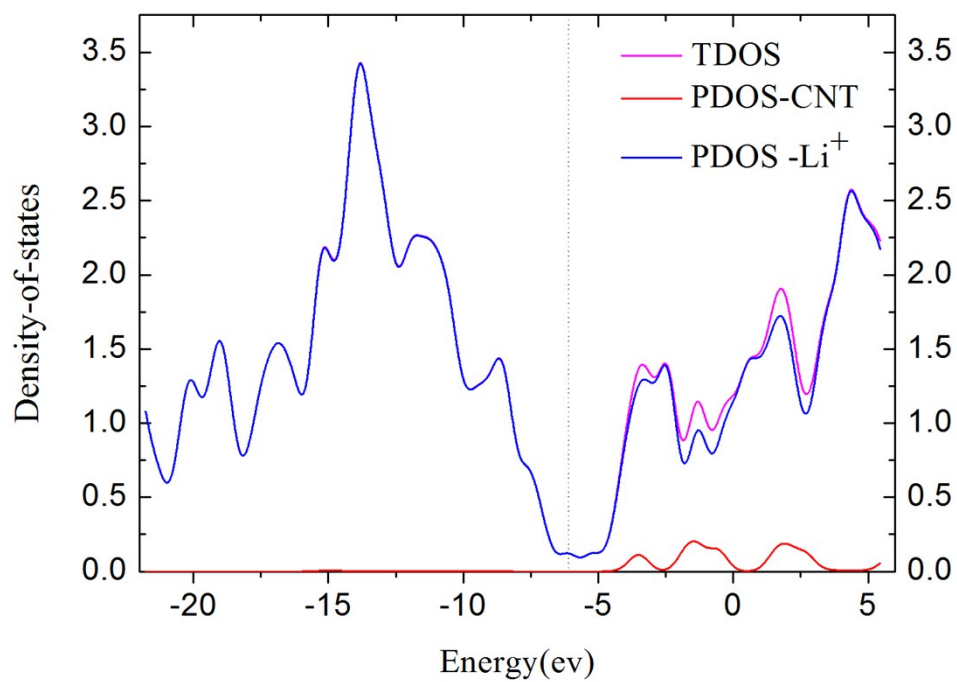


Fig.S2. Molecular orbital of the $\text{Li}^+@(\text{6,6})\text{CNT}$ with isovalue of $0.006 \text{ e}/\text{\AA}^3$ at the lowest unoccupied molecular orbital (LUMO).



Analysis of the molecular orbitals has been further employed to understand the charge exchange between the Li^+ and π electrons of carbons in CNT. We take the (6, 6) CNT with a Li^+ ion adsorbed in the internal wall as an example. The status of the lowest unoccupied molecular orbital (LUMO) of the $\text{Li}^+@CNT$ is displayed in Fig. S2, representing the molecular orbitals with interactions between the Li^+ and CNT. From the LUMO distribution of the $\text{Li}^+@CNT$, we learn that there is an orbital couple between the delocalized π orbital and the unoccupied orbital of the Li^+ .

Fig. S3. The total density of states (TDOS) of $\text{Li}^+\text{@CNT}$ in the internal wall of (6,6) CNT and the partial density of states (PDOS) of Li^+ and CNT.



The valance band of CNT does not change, while conduction band (CB) increases due to the intercalation of Li^+ .

We have performed DFT calculations with two Li⁺/Li adsorbed in and out the (10,10) CNT to roughly illustrate the impact of Li density on the cell voltage. Two different adsorption conditions are taken into consideration, which is shown in Fig. S4.

Fig.S4. Two different adsorption conditions; (a) Two Li⁺ ions are in a straight line separated by two carbon rings. (b) Two Li⁺ ions are irregularly arranged in (10,10) CNT.

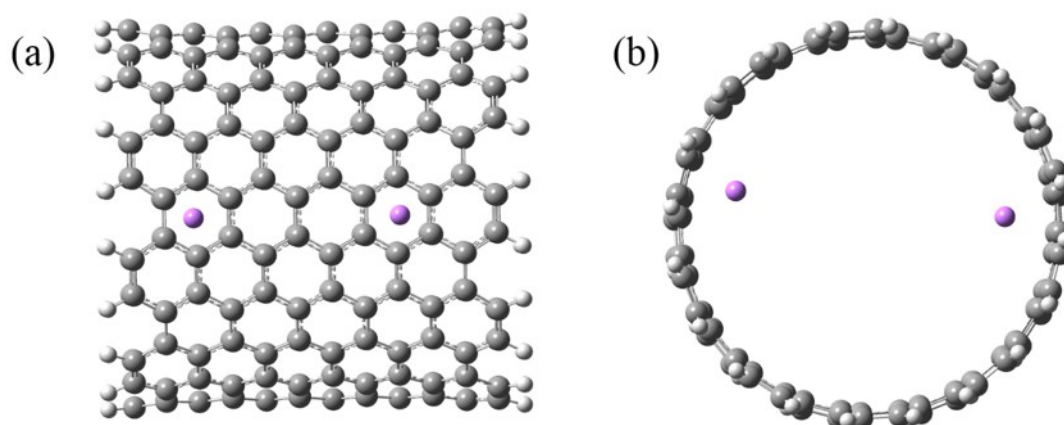


Table S1. The cell voltages for different systems.

	Internal wall		External wall	
	$E_{\text{Li}^+-\pi}$ (kcal/mol)	V_{cell} (V)	$E_{\text{Li}^+-\pi}$ (kcal/mol)	V_{cell} (V)
1-Li	-57.1	1.35	-54.7	1.45
2-Li- Ir ^a	-81.4	1.30	-83.8	1.78
2-Li- St ^b	-73.6	0.99	-71.5	1.38

^aTwo Li⁺ ions are arranged in a straight line separated by two carbon rings.

^bTwo Li⁺ ions are irregularly arranged in (10,10) CNT.

The internal energy is expressed by $\Delta E_{\text{tot}} = E_{\text{Li}} + E_{\text{Li}^+@ \text{CNT}} - E_{\text{Li}@ \text{CNT}} - E_{\text{Li}^+}$, from Table S1.,

we can see that the Li⁺- π interaction is still in favorable for the internal energy. Based on the Nernst equation, the Li⁺- π interaction is still beneficial to the cell voltage. In addition, the cell voltage is larger when two Li⁺ ions adsorbed on the external wall than that on the internal wall, which is consistent with the result with one Li⁺ intercalation. With the increase of Li⁺ density, the difference of cell voltage between the external wall and internal wall is larger. Overall, our main conclusions don't change, for example: the Li⁺- π interaction is beneficial to cell voltage and the cell

voltage is larger when Li^+ adsorbed on the external wall than that on the internal wall. We also note that the impact of Li^+ - π interaction on the voltage becomes complex when multiple lithium ions intercalate into the CNTs. More study of Li density impact on the voltage will be included in an extension paper.